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Isolation and X-ray Crystal Structure of Ph_3SnO_2SePh: The First Example of an Organotin Ester of Phenylseleninic Acid

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Recently, several new structural types for organotin compounds have been discovered. These include the "drum", "cube", "ladder", "butterfly", "O-capped cluster", and "crown" forms as described in several reviews.[2] These organotin clusters are assembled by a reaction of an appropriate mono- or diorganotin derivative with carboxylic or phosphorous-based acids. They contain a repeating distannoxane unit, and alternate Sn atoms in the clusters are linked via bridging carboxylate or phosphate ligands. It is noted that the ultimate structures adopted by these compounds are extremely sensitive to the nature of the ligand. Thus, while the reaction of *n*-butylstannoic acid with various carboxylic acids leads primarily to either drum or ladder motifs,[3] reaction with phosphinic acids affords cubes[4] or O-capped clusters.[5] It seems likely that other structural forms could by synthesized by a subtle variation of the ligand, and hence it was thought worthwhile to explore the reactivity of an organoseleninic acid with various organotin precursors. Initially the reaction between phenylseleninic acid and triorganotin oxides was investigated in order to examine whether the $^-O_2SePh$ moiety could function as a bridging ligand between neighboring Sn centers. This report describes the synthesis and X-ray crystal structure of an unprecedented triorganotin ester of an organoseleninic acid, Ph_3SnO_2SePh.

Experimental Section

General Data. Bis(triphenyltin)oxide was obtained commercially (Aldrich) and used without further purification. Phenylseleninic acid was obtained in the following manner: diphenyl selenide (synthesised using Se metal and PhMgBr in the literature procedure[6]) was oxidized using H_2O_2 and the product obtained, $PhSeO_2H$, was purified according to the literature method.[7] C and H analyses were carried out at the Central Drug Research Institute, Lucknow, India, and at the Department of Chemistry, University of Calgary, Alberta, Canada.

Synthesis of Ph_3SnO_2SePh. Bis(triphenyltin)oxide (0.50 g, 0.70 mmol) was dissolved in 100 cm^3 of dry benzene [*Caution*! Benzene is a known carcinogen] to which phenylseleninic acid (0.27 g, 1.42 mmol) was added. The reaction mixture was heated under reflux for 4 h with a Dean–Stark evaporator used to distill off water azeotropically. Removal of solvent afforded a solid which was sparingly soluble in most solvents including benzene. The product was recrystallized by dissolving a small portion in hot benzene and allowing the solvent to cool slowly; the crystals obtained had a melting point of 511–513 K. Anal. Calcd for $C_{24}H_{20}O_2SeSn$: C, 53.57; H, 3.75. Found: C, 53.45; H, 3.82.

Collection and Refinement of X-ray Data. Intensity data for a colorless crystal of Ph_3SnO_2SePh (0.35 × 0.16 × 0.16 mm) was measured at room temperature (295 K) on an Enraf-Nonius CAD4*F* diffractometer fitted with Cu Kα radiation (graphite monochromator), $\lambda = 1.5418$ Å. The ω–2θ scan technique was employed to measure data to a maximum Bragg angle of 75.0°; no significant decomposition of the crystal occurred during the data collection. Lorentz and polarization corrections were applied[8] as was an analytical absorption correction such that the maximum and minimum transmission factors were 0.317 and 0.072, respectively.[9] Crystal data are summarized in Table I. The structure was solved from the interpretation of the Patterson map and refined by a full-matrix least-squares procedure based on *F*.[9] Anisotropic thermal parameters were employed for all non-H atoms and H atoms were included in the model at their calculated positions. A weighting scheme of the form $w = [\sigma^2(F) + |g|F^2]^{-1}$ was introduced and the refinement continued until convergence; final refinement details are listed in Table I. The analysis of variance showed no special features, indicating that an appropriate weighting scheme had been employed.

Fractional atomic coordinates are listed in Table II, the numbering scheme employed is shown in Figure 1, which was drawn with the ORTEP[10] program at 25% probability ellipsoids, and selected interatomic bond distances and angles are listed in Table III. Scattering factors for all atoms were those incorporated in SHELX76.[9]

Results and Discussion

The reaction of bis(triphenyltin)oxide with phenylseleninic acid proceeds smoothly and in an analogous fashion with many carboxylic acids:[8]

$$Ph_3Sn{-}O{-}SnPh_3 + 2PhSe(O)OH \rightarrow 2\underset{1}{Ph_3SnO_2SePh} + H_2O$$

The product (**1**) has been fully characterized by a single-crystal X-ray diffraction study; the molecular structure is shown in Figure 1, and selected interatomic parameters are listed in Table III.

The Sn atom in **1** exists in a slightly distorted trigonal bipyramidal geometry with the basal plane being defined by the three phenyl groups and the axial positions being occupied by two O atoms derived from two symmetry related, bridging $^-O_2SePh$ ligands; the sum of the trigonal angles is 360°, the axial angle, O(1)–Sn–O(2)′ (symmetry operation: $0.5 - x$, $0.5 + y$, z), is 175.9 (2)°, and the Sn atom lies in the plane of the three C atoms within experimental error. The $^-O_2SePh$ ligand symmetrically bridges two Sn atoms forming indistinguishable Sn–O bond distances (Sn–O(1) = 2.225 (5) and Sn–O(2)′ = 2.223 (4) Å), which leads to a polymeric array as shown in the lower view of Figure 1. The symmetrical bridging mode of coordination of the $^-O_2SePh$ ligand is reflected in the experimentally equivalent Se–O(1) and Se–O(2) bond distances of 1.682 (5) and 1.696 (5) Å, respectively. The Se atom geometry is pyramidal owing to the presence of a stereochemically active lone pair of electrons; there is no evidence of an interaction between the Sn and Se atoms.

The structure found here for Ph_3SnO_2SePh may be compared to those for the closely related carboxylate derivatives, $R_3Sn(O_2CR')$, for which there is a wealth of structural data,[2c] and to those for the less numerous phosphate derivatives.[11–13] There are two major structural forms for compounds of the general formula $R_3Sn(O_2CR')$. The first is molecular and features

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Table I. Crystal Data for Ph_3SnO_2SePh

formula	$C_{24}H_{20}O_2SeSn$	μ, mm^{-1}	11.312
fw	538.1	θ limits, deg	2.0–75.0
cryst syst	orthorhombic	*hkl* range	$+h, +k, -l$
space group	*Pbca*	no. of data collcd	5349
	D_{2h}^{15}, No 61)	no. of unique data	4418
a, Å	14.214 (1)	R_{amal}[a]	0.026
b, Å	11.801 (1)	no. of data ≥ 2.5 $\sigma(I)$	2602
c, Å	25.597 (1)	R	0.038
V, Å^3	4293.6	g	0.0078
Z	8	R_w	0.043
D_{calc}, g cm^{-3}	1.665	ρ_{max}, e Å^{-3}	0.37
$F(000)$	2112		

[a] Where $R_{amal} = (\sum\{N\sum[w(F_{mean} - |F_o)^2]\}/\sum[(N-1)\sum w|F_o|^2)])^{1/2}$ where the inner summation is over N equivalent reflections averaged to give F_{mean}, the outer summation is over all unique reflections, and the weight, w, is taken as $[\sigma(F_o)]^{-2}$.

Table II. Fractional Atomic Coordinates (×10^5 for Sn, Se; ×10^4 for Other Atoms) for Ph_3SnO_2SePh

atom	x	y	z
Sn	20611 (3)	64353 (3)	13625 (2)
Se	36037 (5)	41647 (6)	9797 (3)
O(1)	2900 (3)	4846 (4)	1404 (2)
O(2)	3864 (3)	2949 (4)	1302 (2)
C(1)	823 (5)	5414 (5)	1344 (3)
C(2)	154 (5)	5590 (7)	979 (4)
C(3)	–640 (7)	4906 (9)	943 (4)
C(4)	–737 (7)	4012 (8)	1287 (4)
C(5)	–78 (7)	3835 (7)	1670 (4)
C(6)	713 (6)	4541 (6)	1700 (3)
C(7)	2631 (6)	6950 (6)	2095 (3)
C(8)	2286 (7)	7874 (7)	2356 (3)
C(9)	2670 (9)	8210 (10)	2834 (4)
C(10)	3363 (9)	7604 (11)	3046 (4)
C(11)	3744 (10)	6684 (11)	2791 (4)
C(12)	3361 (8)	6339 (8)	2320 (4)
C(13)	2696 (5)	6848 (6)	632 (3)
C(14)	2482 (6)	6252 (7)	188 (3)
C(15)	2906 (6)	6497 (8)	–288 (3)
C(16)	3564 (7)	7353 (9)	–318 (3)
C(17)	3805 (7)	7946 (8)	129 (3)
C(18)	3372 (5)	7687 (7)	595 (3)
C(19)	4774 (6)	4957 (6)	1091 (3)
C(20)	5242 (7)	4904 (10)	1540 (5)
C(21)	6076 (7)	5508 (9)	1591 (6)
C(22)	6428 (9)	6115 (9)	1175 (7)
C(23)	5938 (8)	6157 (9)	722 (6)
C(24)	5108 (7)	5586 (8)	664 (4)

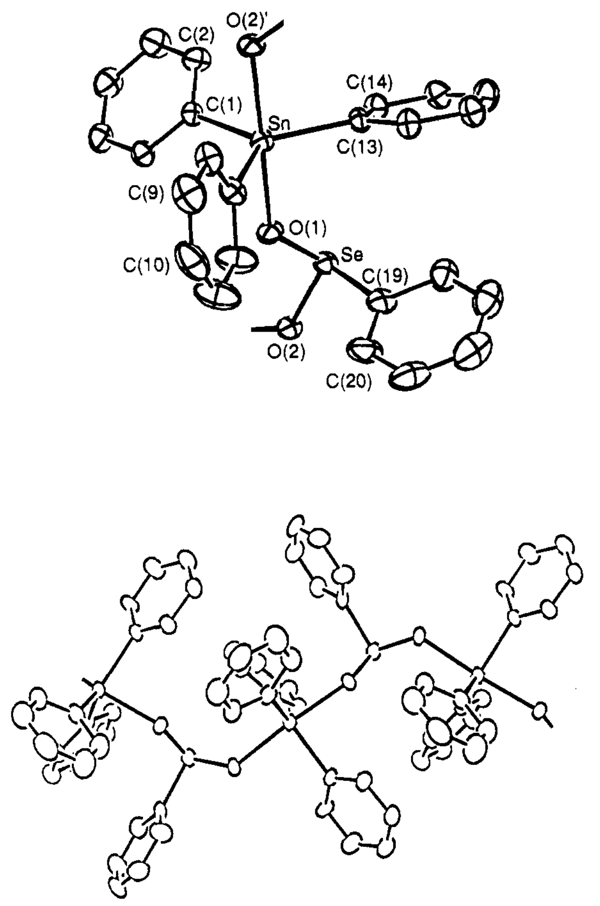

Figure 1. Molecular structure and crystallographic numbering scheme for Ph_3SnO_2SePh (upper view) and a portion of the polymeric chain in the lattice (lower view).

Table III. Selected Bond Distances (Å) and Angles (deg) for Ph_3SnO_2SePh

Sn–O(1)	2.225 (5)	Sn–O(2)′[a]	2.223 (4)
Sn–C(1)	2.133 (6)	Sn–C(7)	2.132 (7)
Sn–C(13)	2.132 (6)	Se–O(1)	1.682 (5)
Se–O(2)	1.696 (5)	Se–C(19)	1.929 (8)
O(1)–Sn–O(2)′	175.9 (2)	O(1)–Sn–C(1)	88.1 (2)
O(1)–Sn–C(7)	89.7 (3)	O(1)–Sn–C(13)	90.5 (2)
O(2)′–Sn–C(1)	88.0 (2)	O(2)′–Sn–C(7)	93.3 (3)
O(2)–Sn–C(13)′	90.3 (2)	C(1)–Sn–C(7)	119.6 (3)
C(1)–Sn–C(13)	117.3 (3)	C(7)–Sn–C(13)	123.1 (3)
O(1)–Se–O(2)	102.7 (2)	O(2)–Se–C(19)	98.6 93)
O(1)–Se–C(19)	100.7 (3)	Sn–O(1)–Se	133.7 (3)
Sn–O(2)′–Se′	125.8 (3)		

[a] Primed atoms are related by the symmetry operation $0.5 - x$, $0.5 + y$, z.

essentially distorted tetrahedral Sn centers with additional, but usually weak interactions to the non-coordinating O atom which increases the coordination number at the Sn atom. The second structural type is polymeric with distorted trigonal bipyramidal centers, i.e. the *trans*-R_3SnO_2 form, and is much the same as reported here for **1**. For this latter type the Sn–O bond distances are normally disparate with the most symmetrical being found in the structure of another triphenyltin compound, i.e. Ph_3SnO_2CH, in which the Sn–O bond distances are 2.219 (6) and 2.317 (6) Å for molecule 1 and 2.219 (6) and 2.318 (5) Å for molecule 2.[14] Although the triorganotin phosphates have received considerably less attention that the $R_3Sn(O_2CR')$ compounds described above, X-ray crystallographic studies have revealed remarkably different structures.[11-13] Structures based on hexameric rings, owing to the presence of bridging phosphate ligands, are found for $\{Ph_3Sn[O_2P(OPh)_2]\}$[11] and $\{Ph_3Sn[O_2P(OMe)Me]\}$[12] whereas infinite helical chains (also due to bridging ligands) are found the lattice of $\{Me_3Sn[O_2P(OH)Ph]\}$.[13] In each of these structures the Sn atom exists in a trigonal planar geometry with the organic substituents defining the trigonal plane.

In conclusion, the phenylselenic acid reacts in a facile manner with triorganotin oxides, and it has been shown that the $^-O_2SePh$ ligand can function as an effective bridging group. These studies are being extended to other, more complex cluster formations.

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Supplementary Material Available: Listing of anisotropic thermal parameters, hydrogen atom parameters, and all interatomic bonding parameters (Tables S(1)–S(3)) (3 pages). Ordering information is given on any current masthead page.

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